



Study of nitrile-containing proton exchange membranes prepared by radiation grafting: Performance and degradation in the polymer electrolyte fuel cell



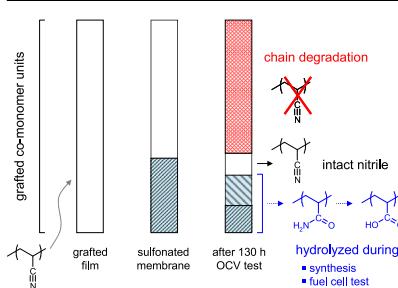
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HIGHLIGHTS

- Radiation grafted membranes were prepared using styrene and nitrile co-monomers.
- Nitrile co-monomers used were acrylonitrile (AN) and methacrylonitrile (MAN).
- Nitrile containing membranes showed enhanced stability in the OCV hold tests.
- The improved stability is due to the enhanced gas barrier properties of the membranes.
- AN is susceptible to hydrolysis, which leads to a loss of the stabilizing property.

GRAPHICAL ABSTRACT



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ABSTRACT

The fuel cell performance and durability of three kinds of styrene based radiation grafted membranes are investigated and compared in the single cell. The styrene/methacrylonitrile (MAN) co-grafted membrane exhibits the best performance among the tested radiation grafted membranes. The accelerated tests under open circuit voltage (OCV) conditions and *post-mortem* analysis demonstrate that the nitrile-containing membranes exhibit significantly enhanced durability compared to the pure styrene grafted membrane, which is associated with the reduced gas crossover rates and attributed to the improved gases barrier properties due to the polarity of the nitrile group. To understand the influence of each functional group in the co-monomer units, both styrene/MAN and styrene/acrylonitrile (AN) co-grafted membranes are evaluated in a set of tests at OCV. The degrees of loss of the graft components are subsequently quantitatively analyzed based on FTIR spectra, showing a comparable decomposition rate of grafted styrene units, but more loss of nitrile in case of the styrene/AN co-grafted membrane. The styrene/AN co-grafted membrane, with AN lacking protection at the α -position in contrast to MAN, is found to be susceptible to significant hydrolysis, directly leading to an accelerated degradation in the late stages of the 130 h OCV test and inhomogeneous in-plane degradation.

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1. Introduction

The polymer electrolyte fuel cell (PEFC) is a promising candidate as an energy conversion device for many applications, such as electric vehicles, distributed power stations, consumer electronics

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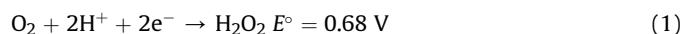
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etc. [1]. A thin organic proton exchange membrane is used in this kind of fuel cell, playing the dual role of electrolyte and separator for gases and electrons. The electron-beam or γ -ray induced radiation grafting provides a versatile tool to prepare proton exchange membranes owing to the wide choice of monomers available for grafting [2]. Moreover, radiation grafted poly(styrene sulfonic acid) (PSSA) membranes are potentially cost-effective alternatives to perfluoroalkylsulfonic acid (PFSA) membranes, such as the Nafion® series [3]. In essence, radiation grafting is a film modification technique, which consists of the addition of a second polymer, the “graft” component, into a preformed base polymer film to introduce a desired property, for instance proton conductivity [4]. In the process, the base polymer is exposed to ionizing radiation to create “active” sites, such as free radicals or peroxide groups. When the irradiated film is brought into contact with a solution containing monomers amenable to radical polymerization, the active sites initiate polymerization reactions, leading to the formation of grafted chains covalently attached to the base polymer. Often, further reactions are performed after grafting, for instance sulfonation to introduce proton exchange sites. Radiation grafted membranes for fuel cells typically possess a chemically and mechanically robust base polymer, usually a fluoropolymer [5], e.g. poly(ethylene-co-tetrafluoroethylene) (ETFE), and hydrocarbon grafted chains composed of sulfonated polystyrene or its copolymers synthesized by co-grafting of styrene with selected co-monomers [2,6,7]. Unfortunately, due to the vulnerable α -hydrogen, the styrene based membrane is prone to degradation of the styrenesulfonic acid (SSA) units and thus the loss of proton conductivity under fuel cell conditions [8–11].

Advanced radiation grafted membranes with improved durability and performance have been investigated and developed through optimizing the properties of base films [12,13], replacing styrene with more stable combination of monomers [14,15] and introducing an optimized crosslinked network into the membranes [16]. In our previous research, methacrylonitrile (MAN) was used as co-monomer to promote the grafting of α -methylstyrene (AMS), and the obtained membranes displayed significantly higher durability in the fuel cell compared to pure styrene grafted membranes [17], and good fuel cell performance that was very close to that of Nafion® NR212 [18]. Furthermore, under constant current density (500 mA cm^{-2}) operation, a fuel cell assembled with styrene/MAN co-grafted membrane exhibited longer lifetime than a fuel cell using the membrane grafted with only styrene [19]. Recently, a 2'400 h durability test was performed in a 6-cell stack at 80°C under dynamic load conditions, and showed that the durability of optimized radiation grafted membranes comprising sulfonated α -methylstyrene as protogenic unit can even exceed that of state-of-the-art Nafion® XL-100 [20]. There is, however, considerable interest in further developing membranes based on grafted styrene, owing to its superior grafting kinetics compared to that of α -methylstyrene. Yet, the durability, especially chemical stability, of styrene based co-grafted membranes has not been comprehensively investigated and understood. In addition, the influence of co-monomers, such as MAN, on the deterioration of radiation grafted membranes still remains an open question and worthy of investigation for further discussing aging mechanisms and tailoring the properties of membranes. To answer this question and promote the understanding of the influence of each functional group in the MAN units, such as α -methyl and nitrile, we co-graft styrene with acrylonitrile (AN) for a comparison with styrene/MAN co-grafted membranes in terms of performance and durability.

It has been widely accepted that hydrogen peroxide (H_2O_2) and membrane-degrading species, such as $\text{HO}\bullet$, $\text{HOO}\bullet$, and $\text{H}\bullet$, are generated in the fuel cell due to the crossover of reactant gases through the membrane, which induce membrane chemical

degradation of both PFSA and PSSA based membranes [10,21–23]. Therefore, the gas crossover rate is critical for the chemical degradation mechanism of a polymer electrolyte membrane in the PEFC configuration. The chemical stability of radiation grafted membranes in this study is examined by accelerated stress tests in the presence of H_2 and O_2 and under conditions of OCV, which is often used as an accelerated stress protocol to assess chemical stability of the membranes [24]. Since there are no fuel and oxidant being consumed electrochemically at OCV, gas crossover through the membrane is potentially increased, leading to increased formation of peroxide and radicals that attack the membrane [25,26]. It is worth mentioning that the two-electron reduction of O_2 (cf. Equation (1)), which is another possible mechanism for generating the radical precursor H_2O_2 at the cathode independent of the gas crossover, does not play a significant role during OCV hold tests owing to, 1) the absence of faradaic current, and 2) the high cathode potential of $>0.9 \text{ V}$ [10]. However, the mechanism shown in Equation (1) is likely to occur at the anode, depending on O_2 permeation. Hence, with respect to the OCV durability test, gas barrier properties of proton exchange membranes are a significant factor for the formation of membrane-degrading species.



The hydrolysis of nitrile in the styrene/AN co-grafted membranes has been observed during the preparation of membranes [27]. However, the influence of hydrolysis on membrane durability has not been investigated yet. This is likely to be very interesting, because the hydrolysis process in the nitrile-containing membranes can convert the nitrile group to the carboxylic acid group, which is susceptible to attack by $\text{HO}\bullet$, as it has been reported in case of PFSA membranes with imperfections in the form of $-\text{COOH}$ end-groups [28]. To understand the influence of hydrolysis on membrane durability, it is thus important to quantify the fraction of nitrile groups converted to amide and carboxylic acid. We have developed a calculation method, based on integrating the characteristic IR-bands, to determine the degree of the nitrile hydrolysis after the fuel cell test (cf. supplementary data).

In this study, we investigate the effect of nitrile-containing co-monomers (MAN, AN) on fuel cell performance and membrane chemical degradation through testing styrene/MAN and styrene/AN co-grafted membranes in comparison to a pure styrene grafted membrane (Fig. 1) in the single fuel cell. The online measurement of cell voltage and membrane resistance as a function of run time over the OCV test period will be presented, and *post-mortem* tests are used to evaluate the durability of each kind of membrane. The gas permeation rates of the different radiation grafted membranes with and without nitrile units are measured, and their contribution for improving membrane stability will be elucidated. The degree of membrane degradation and the degree of nitrile hydrolysis are quantified to show the evolution of the decomposition of SSA units

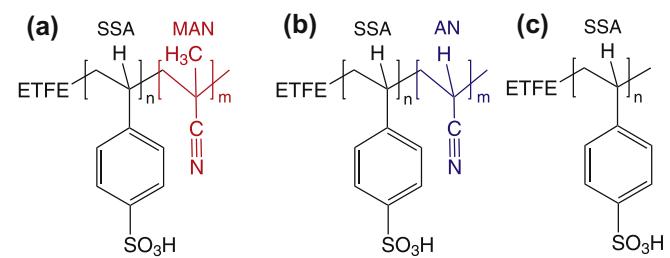


Fig. 1. Schematic of the chemical composition of the membranes used in this study. (a): styrene/MAN co-grafted membrane (grafted S-MAN); (b): styrene/AN co-grafted membrane (grafted S-AN); (c): pure styrene grafted membrane (grafted S).

as a function of time, and to analyze the importance of nitrile units and the impact of hydrolysis on membrane durability under OCV conditions.

2. Experimental

2.1. Membrane preparation and *ex situ* properties

The membranes were prepared by co-grafting styrene (S) and MAN or AN into pre-irradiated ETFE base film (25 μm thickness) followed by sulfonation. The base films (Tefzel® 100LZ) purchased from Dupont were washed in ethanol and dried in vacuum at 60 °C. Then they were electron beam irradiated with a dose of 1.5 kGy for co-grafting styrene with MAN and 3 kGy for co-grafting styrene with AN, respectively, at Leoni Studer AG (Däniken, Switzerland) and subsequently stored at –80 °C until they were grafted. Note that the dose for co-grafting styrene with AN was twice as much as for co-grafting styrene with MAN due to the inferior grafting kinetics of the styrene/AN system [29]. The grafting solutions comprised 20 vol% monomer (mixture of styrene/MAN and styrene/AN with a molar ratio of 2/3, respectively), 70 vol% isopropanol and 10 vol% deionized water. A stainless steel reactor, in which the pre-irradiated ETFE film and grafting solution were loaded, were purged with N₂ for 1 h to remove oxygen before starting the reaction. Following these steps, the reactor was placed in a water bath at a thermostatically controlled temperature of 60 °C for 13 h to co-graft styrene with MAN and for 75 min to co-graft styrene with AN, respectively, to obtain a graft level of around 40%. The grafted films were then removed from the reactor, washed with toluene to remove homopolymer and dried under vacuum at 80 °C overnight, after which the mass based graft level can be determined as defined in our previous work [30]. Subsequently, grafted films were sulfonated with 2 vol% chlorosulfonic acid as sulfonating agent in dichloromethane at room temperature for 5 h, followed by swelling in deionized water at 80 °C for 8 h.

The composition of the grafted films was determined by FTIR spectroscopy using a Perkin Elmer FTIR System 2000 spectrometer. The ion exchange capacity (IEC) was measured by titration. The conductivity of the water swollen membranes was measured by AC impedance spectroscopy (Zahner IM6, Zahner Messtechnik, Kronach, Germany) at room temperature. The thickness of the membranes was measured in water swollen state using a digital thickness gauge (MT12B Heidenhain, Germany), taking five repeat measurements. The hydration number of the membrane is defined as the number of water molecules per sulfonic acid site. It is calculated from the IEC and the water uptake, which is defined as the mass of water absorbed by the membrane divided by the dry weight. The details of the used characterization methods are available elsewhere [30]. The relevant *ex situ* properties of membranes are shown in Table 1. For comparison, a fixed IEC of ~1.5 mmol g^{−1} was chosen as a reference point for all radiation grafted membranes. A molar fraction of around 0.5 for nitrile groups on the grafted polymer chains was selected to study and compare the behavior of the membranes co-grafted with MAN and AN.

2.2. PEFC single cell preparation and operation

The membrane electrode assembly (MEA) was of standard specifications designed for use in a particular single cell. Hot pressing (110 °C/40 kN/180 s) was used to laminate membrane, subgaskets and electrodes together to form an MEA. Carbon-paper based gas diffusion electrodes (GDE) with a platinum loading of 0.4 mg cm^{−2} (type: ELE 0162) were purchased from Johnson Matthey Fuel Cells and used for both anode and cathode, respectively. The active area on each GDE was 16 cm². The MEA, together with gaskets, was compressed between two graphite flow filed plates with co-flow parallel gas channels to make a single cell.

The cell was operated with a computer controlled fuel cell testing system comprising a LabVIEW (National Instruments) program for system control and data acquisition. Pure hydrogen and oxygen were used as fuel and oxidant, respectively. Hydrogen was fed to the anode at 600 mL min^{−1} and oxygen was fed to the cathode at 600 mL min^{−1}. Before being fed to the cell, the gases were supplied to controlled evaporator mixers (CEMs) (Bronkhorst AG, W-202A-133-K) to be humidified with deionization water. The backpressures (typically at 2.5 bar_a) of the gases were regulated with pressure controllers that were located downstream of the gas outlets of the cell. All experiments were carried out at a cell temperature of 80 °C. Before online characterization, the cell was conditioned at 500 mA cm^{−2} for 20 h under fully humidified conditions.

2.3. Electrochemical hydrogen permeation measurements

The mechanical integrity and gas permeability of membranes can be assessed via a measurement of the hydrogen crossover rate based on the single cell configuration described above. Through an electrochemical method [31,32], hydrogen crossover across the membrane was evaluated at 80 °C, 2.5 bar_a (backpressure at both sides) and full humidification conditions. Fully humidified pure hydrogen and nitrogen were fed to the anode and the cathode, respectively, at 600 mL min^{−1} each. The hydrogen crossover rate was evaluated with the cell operated in H₂/N₂ mode as a diffusion-limited hydrogen oxidation current density in the range of 200–800 mV.

2.4. Open circuit voltage (OCV) durability tests

Durability tests of the single cell were carried out at 80 °C under open circuit conditions. H₂ and O₂, both fully humidified in the CEMs, were fed to the anode and cathode, respectively, at 600 mL min^{−1} each and at a backpressure of 2.5 bar_a. *In situ* characterization of the single cell was carried out by means of online measurements of cell voltage and high frequency resistance (HFR) as a function of run time. The HFR was measured with an AC milliohm meter (model 3566, Tsuruga, Japan) at a fixed frequency of 1 kHz. Before and after OCV durability tests, the characterizations of cell performance and hydrogen crossover measurements were carried out for a comparison and degradation evaluation.

Table 1

Ex situ properties of the membranes used in this study. Conductivity and hydration were measured in water swollen state at room temperature.

Composition	Molar fraction of styrene ^a	GL (wt-%)	IEC (mmol g ^{−1})	Thickness (wet) (μm)	Conductivity (mS cm ^{−1})	Hydration (H ₂ O/SO ₃ H)
Grafted S	1	~21	1.42 ± 0.08	37 ± 1	79 ± 21	11 ± 1
Grafted S-MAN	0.53 ± 0.05	~40	1.54 ± 0.06	46 ± 1	86 ± 8	18 ± 2
Grafted S-AN	0.46 ± 0.09	~42	1.69 ± 0.03	45 ± 2	79 ± 8	20 ± 1
Nafion® NR212			1.10 ± 0.02	68 ± 1	107 ± 5	17 ± 1

^a In the graft copolymer.

2.5. Post-mortem analysis based on FTIR

After the OCV durability test, the MEA was taken out of the fuel cell hardware. The electrodes were carefully peeled off the membrane and the surface of the membrane was cleaned from remaining particles of the electrode in a mixture of demineralized water and ethanol. The H^+ ions present in the degraded membranes were exchanged with K^+ ions by immersing the membrane in 0.5 M KCl solution overnight. Membranes can be dried more effectively in K^+ form, which minimizes water interference during FTIR analysis. The active area on the membrane was divided into 12 sections, each of which was probed by the FTIR analysis instrument (Fig. 2), and thus the entire active area could be analyzed.

3. Results and discussion

3.1. Fuel cell performance

The polarization curves after 20 h of cell conditioning have been chosen as a reference point for comparing the fuel cell performance of the different membranes. 20 h is actually a compromise, because during the conditioning period, the unstable membranes (e.g. pure styrene grafted membranes) may suffer already from degradation, while the more stable membranes (e.g. nitrile-containing membranes) need dozens of hours to reach a steady-state performance. The polarization curves for the cells with the membranes used in this study are shown in Fig. 3. In order to make a comparison, we also include data of a cell with a Nafion® NR212 membrane.

The performance of the cells with radiation grafted membranes is close to the performance of the cell with Nafion® NR212 membrane. This result is expected, because the ionic resistances of the radiation grafted membranes, measured by high frequency resistance (HFR), display higher values than that of the Nafion® NR212 membrane. The result of the HFR measurement also correlates well to the conductivities measured *ex situ* (Table 1), where the Nafion® NR212 membrane shows higher ionic conductivity than the radiation grafted membranes.

Regarding the radiation grafted membranes, the order of performance also corresponds to the order of ionic resistances of the membranes, with the styrene/AN co-grafted membrane exhibiting the highest HFR, thereby displaying the lowest performance. However, the ionic resistance is not the only factor affecting fuel cell performance; because the pure styrene grafted membrane and the styrene/MAN co-grafted membrane show similar HFR at high current densities, but different cell voltages. For these two types of membrane, we find the interfacial properties of grafted membranes in contact with the same GDE differ considerably, which also

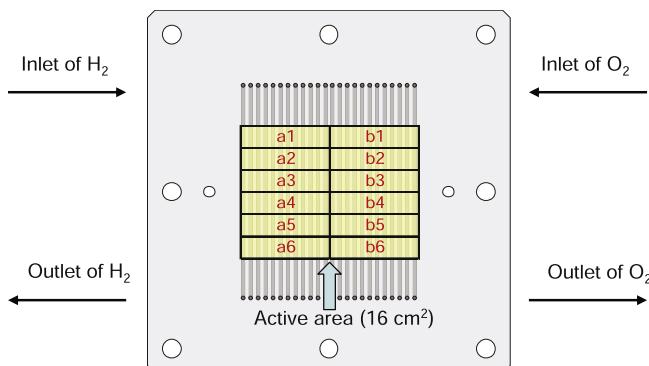


Fig. 2. Layout of the single cell and flow field, with highlighted areas probed in the post-mortem analysis of the membrane using FTIR spectroscopy.

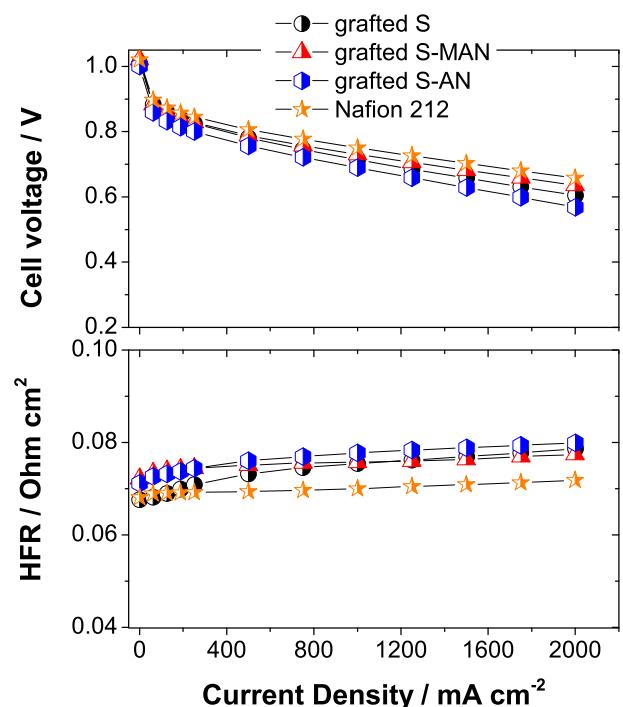


Fig. 3. Polarization curves and high frequency resistance (HFR) of H_2/O_2 (fully humidified) fuel cells at 80 °C and 2.5 bar_a backpressure for membranes indicated in Table 1 and Nafion® NR212.

influence cell performance. The iR-corrected curves, which are dedicated to display the differences in electrochemical reaction polarization by eliminating the factor of ohmic resistance, demonstrate that the pure styrene grafted membrane shows lower performance than the styrene/MAN co-grafted membrane. It indicates the styrene/MAN co-grafted membrane has a higher quality of the membrane–electrode interface. It can be supported by the fact we found that improved interface quality, owing to the polarity of the nitrile group of MAN, somehow induce better adhesion properties between the electrodes and the grafted membrane [33].

3.2. Continuous durability test and stabilizing mechanism of membrane

3.2.1. OCV test and post-mortem analysis

The degradation of fuel cell performance is mainly governed by the stability of membranes under open circuit conditions. With respect to the radiation grafted membranes, measuring membrane resistance *in situ* is the most advisable way of monitoring the membrane degradation during fuel cell tests [34]. We performed the measurement of membrane resistance by the HFR method and were thereby able to follow the variation of the membrane resistance as a function of the operating time during OCV durability tests.

The influence of the membrane composition on the durability of radiation grafted membranes can be seen by comparing the development of the HFR for the radiation grafted membranes in Table 1, which have different composition of the grafts. A number of membranes were tested under OCV conditions and selected results are displayed here for clear illustration due to a large number of points obtained during *in situ* measurements.

The development of cell voltage and HFR for the cells with pure styrene grafted membrane and styrene/MAN co-grafted membrane during 12 h OCV durability test at 80 °C is shown in Fig. 4(a). The

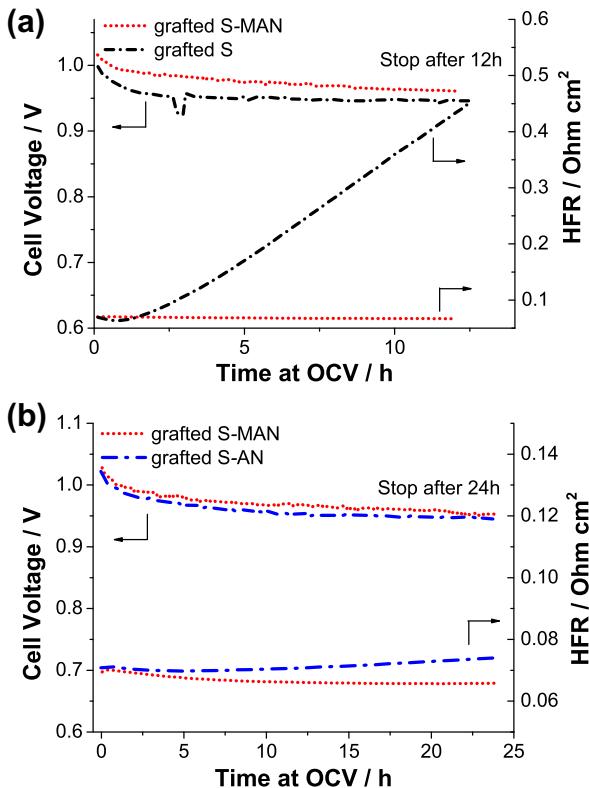


Fig. 4. Cell voltage and membrane resistance (measured by HFR) vs. time of operation of H_2/O_2 fuel cells at $80\text{ }^\circ\text{C}$ for membranes indicated in the legends. (a): 12 h OCV test and (b): 24 h OCV test.

change in the cell voltage of the MEAs with these two membranes remains steady without a significant voltage drop during the test, which implies that there are no physical defects formed during the OCV durability tests. However, they show a very different stability behavior in terms of the increase in HFR. The pure styrene grafted membrane has an initial resistance of $61\text{ m}\Omega\text{ cm}^2$, which increases about 6-fold after 12 h at OCV. The styrene/MAN co-grafted membrane has an initial resistance of $70\text{ m}\Omega\text{ cm}^2$, decreasing slightly to $67\text{ m}\Omega\text{ cm}^2$ over the same period of time. It is speculated that the slight decrease in HFR could be attributed to a difference in the distribution of the sulfonic acid sites between the pristine membrane and the degraded membranes in the early stage of the deterioration process. In the grafted membranes the dispersion of sulfonic acid groups is not entirely homogeneous, and the mobility of a small amount of detached grafted chains trapped in the MEA could possibly improve the homogeneity of the distribution of the sulfonic acid sites, which can potentially increase the ionic conductivity of the degraded membrane in the early stage of the deterioration process. With increased effluence and loss of sulfonic acid groups from the MEA, this effect will vanish as the OCV durability test proceeds.

A similar stability behavior is observed for the membranes shown in Fig. 4(b), where both styrene/MAN and styrene/AN co-grafted membranes were tested under OCV conditions such as shown in Fig. 4(a), but for 24 h. These are nitrile group containing membranes and have the same molar ratio of around 1:1 between SSA and nitrile units, but a difference at the α -carbon of the co-monomer units: MAN has a α -methyl group but AN does not. Within the OCV duration of 24 h, a slow decrease in HFR from $70\text{ m}\Omega\text{ cm}^2$ to $66\text{ m}\Omega\text{ cm}^2$ is found for the cell with the styrene/MAN co-grafted membrane. The resistance of the styrene/AN co-grafted membrane, whose initial value is $72\text{ m}\Omega\text{ cm}^2$, exhibits a small

decrease at the beginning of the OCV test, but then increases with a rather small slope to $74\text{ m}\Omega\text{ cm}^2$ at the end of the test.

At the end of each OCV durability test, the membrane was carefully separated from the electrodes and cleaned from remaining particles of the electrode using the method described above. Then, *post-mortem* analysis was carried out by transmission FTIR. Transmission FTIR can be used to characterize membrane degradation due to the fact that the intensity of the vibrational bands corresponding to functional groups (e.g. SSA and nitrile) diminish during OCV durability tests owing to the chemical attack by membrane-degrading species on the grafted chains followed by detachment from the ETFE backbone.

The FTIR result for the pure styrene grafted membrane and the styrene/MAN co-grafted membrane after 12 h OCV durability test is displayed in Fig. 5(a), which shows the IR spectra of the membranes in the range of $1300\text{--}2300\text{ cm}^{-1}$ before and after the OCV durability test. The bands at 1494 cm^{-1} and 1600 cm^{-1} (assigned to aromatic skeleton stretch vibration) completely vanish in case of the pure styrene grafted membrane after the test, while a change of those bands is hardly seen in the spectrum of the styrene/MAN co-grafted membrane. This result is in agreement with the dramatic increase in HFR measured for the pure styrene grafted membrane and rather stable HFR of the styrene/MAN co-grafted membrane over the test.

The FTIR results for the styrene/AN co-grafted membrane and styrene/MAN co-grafted membranes before and after the 24 h OCV durability test is displayed in Fig. 5(b). The good stability of both kinds of nitrile-containing membranes found in the evolutions of their HFR during testing can be confirmed by the fact that the

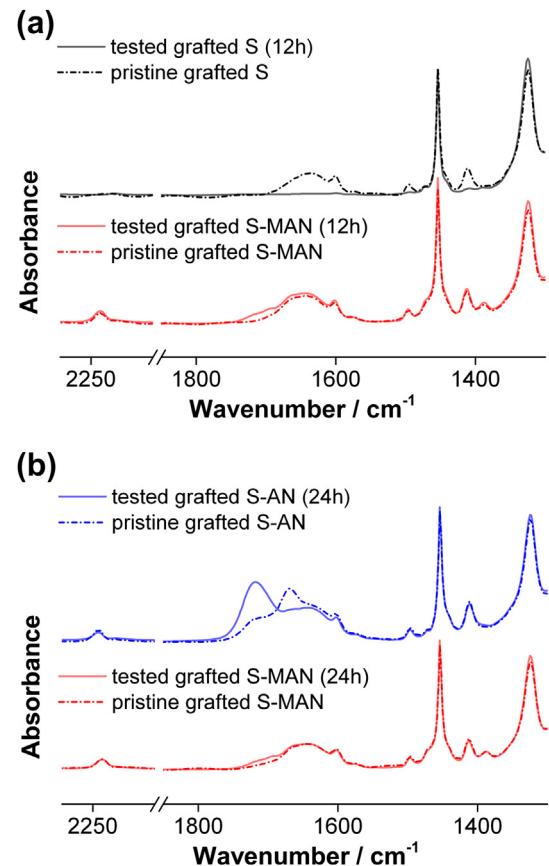


Fig. 5. FTIR spectra of the pristine and tested membranes (composition indicated in the legends). (a) corresponds to 12 h OCV tests, while (b) corresponds to 24 h OCV tests.

Table 2

H_2 crossover rate (expressed as current density) measured at the beginning of test after cell conditioning at 80 °C and 2.5 bar_g backpressure for membranes indicated in Table 1. H_2 and N_2 flow rate of 600 mL min⁻¹, fully humidified.

Membrane type	Grafted S	Grafted S-MAN	Grafted S-AN	Nafion® NR212
Current density (mA cm ⁻²)	1.13 ± 0.10	0.84 ± 0.08	0.88 ± 0.10	1.52 ± 0.13

intensities of the absorption bands at 1494 cm⁻¹ and 1600 cm⁻¹, attributed to aromatic vibration of SSA, show a rather small decrease after the test. The spectra of the styrene/AN co-grafted membrane reveal that the nitrile groups are partially hydrolyzed to amide (1670 cm⁻¹) and carboxylic acid (1700 cm⁻¹). In contrast, the hydrolysis of the nitrile in the styrene/MAN co-grafted membrane is negligible, because there is merely a tiny change in the region near 1700 cm⁻¹. Accordingly, the change of the absorption band at 2234 cm⁻¹ (assigned to $-C\equiv N$ vibration) is less significant for the styrene/MAN co-grafted membrane than for the styrene/AN co-grafted membrane. Note that the signature of OH bending vibration of water is also observed in the range of 1630–1600 cm⁻¹.

3.2.2. Gas crossover and stabilizing mechanism

Combining all the information we obtain from Figs. 4 and 5, we can conclude that the nitrile-containing radiation grafted membranes have considerably enhanced durability compared to pure styrene grafted membranes during the OCV test and this is clearly a result of the presence of nitrile groups in the membrane's structure. As discussed in the introduction, since the crossover of reactant gases is a critical factor governing the degradation of membranes under OCV conditions, the hydrogen crossover measurement can offer us a clue to explain the stabilization mechanism. Table 2 summarizes the hydrogen crossover rates (in mA cm⁻²) of all membranes studied in OCV durability tests plus Nafion® NR212 membrane for comparison. The Nafion® NR212 membrane has the highest hydrogen crossover rate (1.52 mA cm⁻²). It is clear that hydrogen crossover rates are lowest for the styrene/MAN and styrene/AN co-grafted membrane with 0.84 mA cm⁻² and 0.88 mA cm⁻², respectively. The hydrogen crossover rate of the pure styrene grafted membrane is 1.13 mA cm⁻², which is 34% higher than that of the styrene/MAN co-grafted membrane and 28% higher than that of the styrene/AN co-grafted membrane, respectively. Although the hydrogen crossover rates of nitrile-containing membranes are only reduced by around one third in comparison with the pure styrene grafted membrane, it is still likely to have a notable effect on membrane degradation at OCV conditions. In another series of OCV hold experiments using pure styrene grafted membranes, we found that a reduction of the relative humidity from 70 to 30% leads to a reduction in hydrogen crossover by 32%, yet the rate of membrane degradation decreases by a factor of 2.5 [35]. A lowering of the relative humidity from 70% to 30% is supposed to increase the concentration of hydrogen peroxide in the MEA [36,37] and thus lead to accelerated degradation in the case of PFSA membranes [32]. However, in the case of PSSA based membranes, the gas crossover seems to be the main factor governing membrane degradation.

The decreased gas crossover can be explained by the following two aspects. Firstly, the increased thickness (cf. Table 1) of nitrile-containing membranes, caused by the higher grafting level required, may to some extent reduce the gas permeation through the membrane. Yet, this does not seem to be the case for styrene/methacrylic acid (MAA) co-grafted membrane that has a similar thickness than the nitrile-containing membranes used in this study, because we observe a higher H_2 crossover rate and fast degradation

under OCV conditions for the styrene/MAA co-grafted membrane [38]. Secondly, extraordinary gas barrier properties of copolymers of styrene and nitrile co-monomers were observed by Salame and Barnabeo et al. and attributed to the intrinsic high polarity of the nitrile group [39,40]. It is reasonable to thereby speculate that the nitrile groups in the grafted chains increase the interaction between polymer chains due to the high polarity and enhance the stiffness of chains and the chain-to-chain binding, which results in a decrease in gas permeability. The high chain-to-chain binding and stiffness can not only restrict the transport of reactant gases across the membrane but also the transport of membrane-degrading species, which are usually formed on the catalyst surface [41], into the bulk of the membrane. As normally the lifetime of membrane-degrading species is short [10], this may also contribute to lowering the rate of chemical attack on the grafted chains.

3.2.3. Degree of degradation and hydrolysis in the continuous OCV tests

Post-mortem analysis can not only analyze membrane degradation qualitatively but also quantitatively. The loss of the graft components can be quantified by integrating the areas of the bands that correspond to the characteristic groups in the grafted chains, such as aromatic ring and nitrile [42].

For the nitrile-containing membranes used in this study, the degradation degree of SSA and the degree of nitrile loss are quantified for a set of continuous OCV durability tests with increasing operating time (24 h, 48 h, 96 h and 130 h) (Fig. 6). It is worth pointing out that four pristine membranes of each category, which were synthesized in the same grafting batch, were used in the individual tests. The degrees of degradation of SSA in both kinds of membrane gradually increase with time, with around 60% of grafted styrene detached from the backbone after 130 h OCV durability test. Moreover, their rates of decomposition of SSA units are comparable within the investigated time domain, which again demonstrates their similar stability. However, the styrene/AN co-grafted membranes consistently show more loss in nitrile units than the styrene/MAN co-grafted membranes, which results in a loss of about 84% grafted nitrile after 130 h. The more pronounced loss of nitrile in the styrene/AN co-grafted membranes is due to the combination of the chemical attack of membrane-degrading species on the grafted chains and the hydrolysis of nitrile groups to amide and carboxylic acid. Another interesting observation from the result of the styrene/MAN co-grafted membranes is that there is a consistency between the degree of SSA degradation and the degree of nitrile loss. It suggests that, for styrene/MAN co-grafted

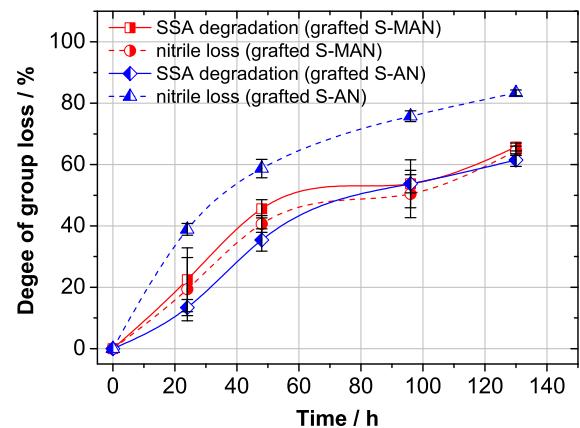


Fig. 6. Degree of loss in the graft component in styrene-g-MAN and styrene/AN co-grafted membranes aged at OCV over different time periods.

Table 3

The calculated degree of nitrile hydrolysis due to testing in styrene/AN co-grafted membranes over different time periods of operation in the fuel cell under OCV conditions.

Duration of AST (h)	24	48	96	130
Degree of hydrolysis (%)	29 ± 6	36 ± 8	48 ± 6	57 ± 5

membranes, the SSA units and nitrile units are decomposed proportionately during OCV tests. Obviously, this is not the case for the styrene/AN co-grafted membranes, where hydrolysis leads to additional nitrile loss.

Since we observed the impact of hydrolysis on the loss of nitrile for styrene/AN co-grafted membranes, it is useful and necessary to quantitatively analyze the degree of hydrolysis of the nitrile units due to testing. In the analysis, we neglect the initial degree of hydrolysis, which takes place during membrane preparation, because we wish to distinguish between hydrolysis resulting from preparation (around 35% [38]) and hydrolysis during testing. Therefore, we define the hydrolysis degree of nitrile groups during the fuel cell test as the content of hydrolyzed nitrile after the test with respect to the remaining content of the initial nitrile co-monomer (cf. supplementary data). The obtained results based on the aged styrene/AN co-grafted membranes are shown in Table 3.

The fate of the nitrile units in the degraded and hydrolyzed membranes with increasing operation time is displayed in Fig. 7. Here, the contribution of nitrile units hydrolyzed during synthesis is included. The pristine membrane only contains the intact nitrile and the nitrile hydrolyzed during preparation, both of which are reduced in proportion with increasing test duration due to degradation of the graft copolymer chain. The fraction of the nitrile hydrolyzed during testing with respect to the originally grafted units remains approximately constant in a range between 17% and 14%. In contrast, the ratio of the nitrile hydrolyzed during testing to the intact nitrile increases with testing time; hence Table 3 shows an increase in the degree of hydrolysis as a function of testing duration. The decomposed fraction increases dramatically with time, the nitrile remaining intact after 130 h only accounts for around 11% of the initially grafted units.

3.3. Intermittent durability tests and impact of hydrolysis

3.3.1. 130 h intermittent OCV test

In parallel with the continuous OCV tests, we also carried out the intermittent OCV tests, where we interrupted the OCV test and performed characterization in terms of fuel cell performance and

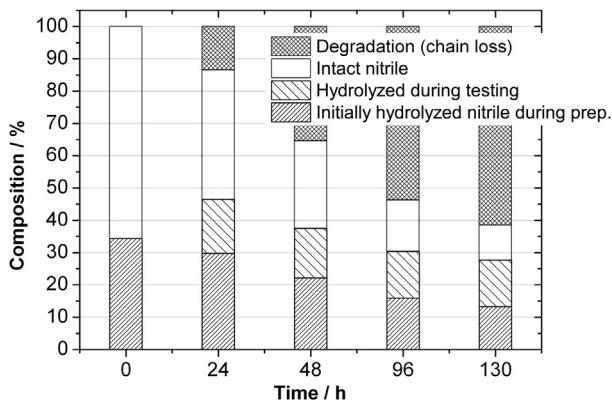


Fig. 7. Analysis of the fate of the original nitrile units in styrene/AN co-grafted membranes aged at OCV in the fuel cell over different time periods of operation.

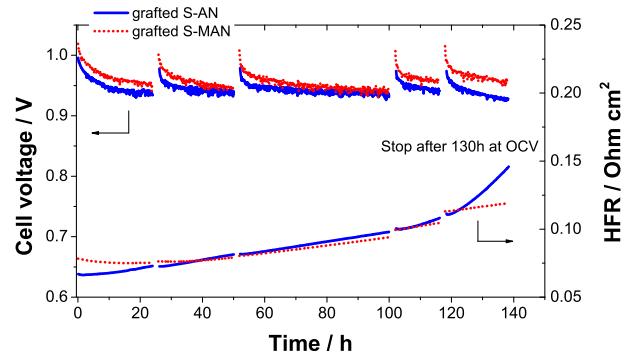


Fig. 8. Variations of cell voltage and HFR of H_2/O_2 cells with a styrene/AN co-grafted membrane and a styrene/MAN co-grafted membrane, respectively, during the intermittent OCV durability tests at $80^\circ C$. H_2 and O_2 were fully humidified. H_2/O_2 flows: $600/600 \text{ mL min}^{-1}$ at 2.5 bar_a backpressure.

membrane mechanical integrity through H_2 crossover current density. The intermittent OCV durability tests were performed (Fig. 8) using MEAs equipped with a styrene/AN co-grafted membrane and a styrene/MAN co-grafted membrane, respectively. The membranes used in the tests were prepared together with the membrane used in the continuous OCV durability tests. The experimental conditions of the intermittent OCV durability tests are the same as those adopted in the continuous tests. The difference is that after a particular time (24 h, 48 h, 96 h and 110 h) the cell was operated with current to characterize the performance of the aged MEA (Fig. 10). Subsequently, hydrogen crossover was measured after O_2 had been replaced by N_2 (Fig. 9). The total accumulated duration at OCV is 130 h.

Fig. 8 shows that the slope of the resistance increase for the styrene/AN co-grafted membrane remains constant within the first four intervals (in total 110 h at OCV), but the deterioration of the membrane is clearly accelerated in the last 20 h, which leads to an increase in HFR to $146 \text{ m}\Omega \text{ cm}^2$ from a initial value of $67 \text{ m}\Omega \text{ cm}^2$. In contrast, the 130 h OCV intermittent test for the styrene/MAN co-grafted membrane witnesses an approximately steady growth of HFR from $78 \text{ m}\Omega \text{ cm}^2$ to $119 \text{ m}\Omega \text{ cm}^2$, indicating that the rate of deterioration of the membrane is roughly constant within the investigated time domain.

Hydrogen crossover current density was measured between two consecutive intervals, and its variation as a function of time is shown in Fig. 9. The hydrogen crossover current density is lowest for both the pristine styrene/AN co-grafted membrane and pristine

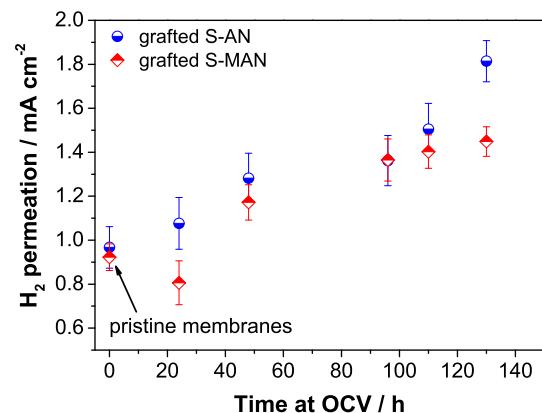


Fig. 9. H_2 crossover rate (expressed as current density) measured intermittently during 130 h OCV tests by an electrochemical method at $80^\circ C$ and 2.5 bar_a backpressure.

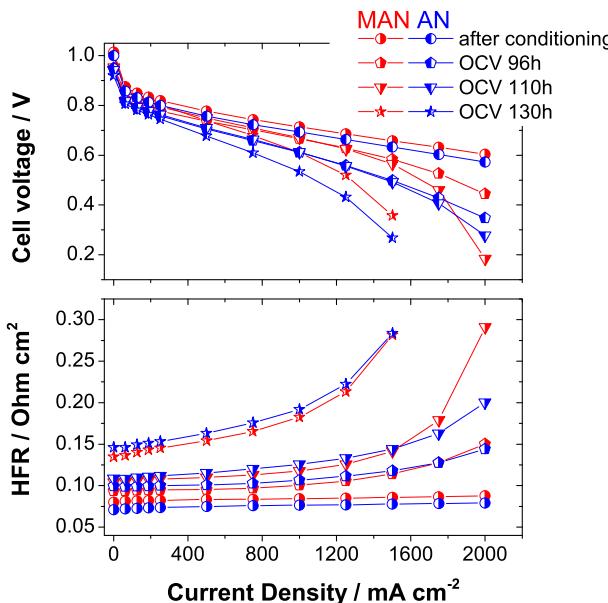


Fig. 10. Evolution of polarization curves of the MEAs with a styrene/AN co-grafted membrane and a styrene/MAN co-grafted membrane, respectively. Cell temperature was 80 °C. H₂ and O₂ (600/600 mL min⁻¹) were fully humidified at 2.5 bar_a.

styrene/MAN co-grafted membrane and gradually increases with ongoing membrane deterioration. Interestingly, for the styrene/AN co-grafted membrane, an acceleration in the increase of gas crossover in the later stages of the OCV durability test is observed, which correlates well to a similar acceleration found in the development of the HFR over the operating time; while the styrene/MAN co-grafted membrane does not exhibit a faster increase in H₂ permeation in the later stages, which is also consistent with the HFR data. This difference can be attributed to the fact that the tested styrene/MAN co-grafted membrane (41.3 ± 0.6 μm in wet state) is thicker than the tested styrene/AN co-grafted membrane (27.5 ± 7.5 μm in wet state), because the styrene/AN co-grafted membrane experiences an accelerated degradation process, leading to severe membrane thinning. In addition, another mechanism is the detachment of grafted chains from the backbone, which can lead to more free volume formed inside the membranes, which facilitates the transport of reactant gases and membrane-degrading species. It can suggest that the degradation of the membrane and the gas crossover are actually mutually influential: on the one hand, the membrane deterioration can lead to an increase in the gas crossover of the membrane; on the other hand, the increased in gas crossover can contribute to an increased formation rate of membrane-degrading species, which further fuels the decomposition of grafted chains and thus enhances the membrane thinning and formation of free volume.

During this intermittent OCV durability test, the cell performance was evaluated after a particular time, as shown in Fig. 10. With reduced proton conductivity of the membrane, the cell shows a clear gradual degradation in terms of performance. We stopped the durability test after the membrane had been subjected to OCV for 130 h, because at this moment the HFR value had increased significantly compared to the initial value, and the MEA was not able any more to provide a reasonable cell voltage at practical current densities. Based on our experience, these phenomena imply that the used membrane has heavily aged.

An increase in the membrane resistance with increasing current density was found in the polarization curves that were performed in the later stages of the OCV durability test, such as after 96 h, 110 h

and 130 h. This phenomenon was investigated before in PFSA membranes (e.g. the Nafion® series) and attributed to a gradient in water content across the membrane, which is determined by the electroosmotic drag of water from anode to the cathode and a limited back-transport of water to the anode [43,44]. Based on the theories proposed previously, the more pronounced degradation (e.g. after 96 h, 110 h and 130 h OCV tests) causes a substantial loss of –SO₃H groups and thus a significant decrease in water content of the membrane. This will result in an insufficient back transport of water to the anode and dehydration of the membrane close to the anode (increase of the resistance at the anode). In contrast, the back-transport of water in the membrane with less degradation is adequate owing to higher water content, and therefore, the back-transport of water to the anode side can compensate the osmotic drag of water from the anode to the cathode at high current densities. Accordingly, the heavier the degradation is, the stronger the increase of membrane HFR will be at a given current density.

3.3.2. Pre-hydrolysis test

In order to investigate the influence of the nitrile hydrolysis on the deterioration of the styrene/AN co-grafted membrane at OCV, we subjected the membrane to significant hydrolysis before starting an OCV durability test. At the beginning of the test, a pristine styrene/AN co-grafted membrane was assembled in a cell purged with H₂ and N₂ at 80 °C. H₂ and N₂, both fully humidified, were fed to the anode and cathode, respectively, at 600 mL min⁻¹ each and at a backpressure of 2.5 bar_a. The cell was operated under these conditions for 336 h (14 days) to hydrolyze the nitrile groups. Afterward, the membrane was disassembled from the cell and characterized with transmission FTIR spectroscopy after cleaning. A 75% loss of nitrile groups was measured, and a decomposition of SSA units could not be detected within the limit of accuracy of the method (10%), which indicates that most of the nitrile groups in the tested styrene/AN co-grafted membrane were hydrolyzed to amide or carboxyl groups during the test. Following that, a new styrene/AN co-grafted membrane was hydrolyzed under identical conditions for 336 h and then degraded at OCV for 72 h. The development of the HFR is shown in Fig. 11 in comparison to the HFR increase of a styrene/AN co-grafted membrane that has not been hydrolyzed before the OCV test.

It is obvious that the heavily pre-hydrolyzed membrane ages much faster than the pristine styrene/AN co-grafted membrane, and the rate of its degradation increases with the time at OCV, which is similar to the degradation process observed in the OCV test for the pure styrene grafted membrane (Fig. 4(a)). These two

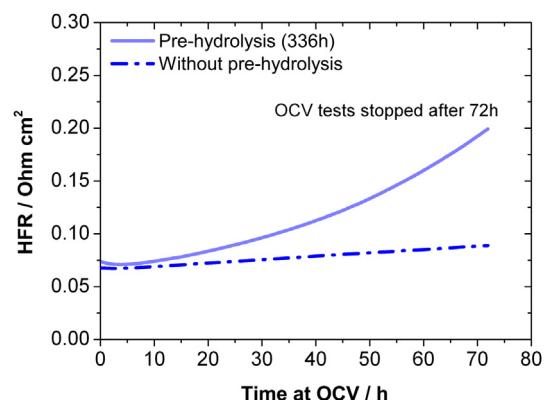


Fig. 11. The effect of nitrile hydrolysis on the increase in the HFR of H₂/O₂ cells with a styrene/AN co-grafted membrane during OCV durability tests at 80 °C. H₂ and O₂ (600/600 mL min⁻¹) were fully humidified at 2.5 bar_a.

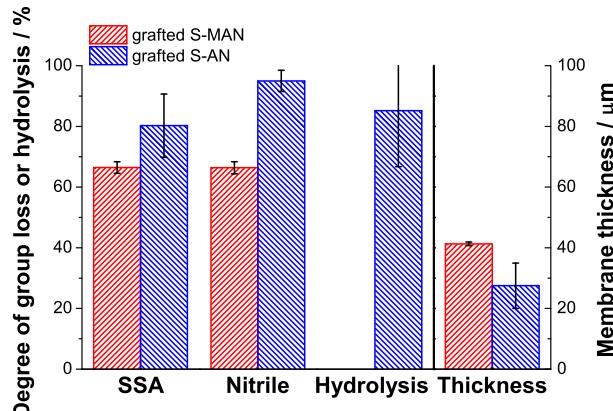


Fig. 12. Calculated degree of SSA degradation, nitrile loss and hydrolysis, and measured thicknesses of the tested membranes after 130 h OCV intermittent tests.

observations actually correlate well with the two phases in the 130 h intermittent OCV test for the styrene/AN co-grafted membrane (Fig. 8): the one without pre-hydrolysis corresponds to the degradation behavior in the first phase (before 110 h) with a constant increase in HFR, while the pre-hydrolyzed one corresponds to the observation in the later stages (after 110 h) where the membrane degradation is accelerated. Again, it suggests that the presence of nitrile can lower the degradation rate of the styrene-based radiation grafted membrane. When the fraction of intact nitrile groups is reduced below a critical level due to both degradation and hydrolysis, the membrane deterioration will be accelerated, approaching a degrading behavior similar to that of the pure styrene grafted membrane. With the data from the 130 h continuous OCV test (Fig. 7), we estimate that the critical fraction of nitrile groups is likely to be in the range below 10%. This is because there is

still about 11% intact nitrile in the membrane after 130 h continuous OCV test, and the results do not show an accelerated process as indicated by online HFR monitoring.

Obviously, the exhaustive loss of the nitrile groups makes the heavily degraded membrane undergo an accelerated deterioration process similar to that found for the pure styrene grafted membrane, which has been proven to be substantially more vulnerable under OCV conditions. Moreover, the presence of carboxylic acid may not contribute to accelerating the deterioration of the membrane, because the hydrolysis has started occurring already in the early stage of degradation in which no accelerated membrane degradation is found. This is different from the chemical degradation mechanism found in the PFSA membranes [28,45]. Therefore, we can conclude that the loss in the protecting effect of the nitrile group in the styrene based radiation grafted membranes is the main factor determining the accelerated degradation in the styrene/AN co-grafted membrane tested under OCV conditions.

3.3.3. Post-mortem analysis for the 130 h intermittent OCV tests

In the 130 h intermittent OCV tests, we see the difference in HFR increase between the styrene/AN co-grafted membrane and the styrene/MAN co-grafted membrane. According to the result from the pre-hydrolysis test, this can be associated with the difference in the resistance against hydrolysis between these two types of membrane, as indicated in the *post-mortem* FTIR spectrum (Fig. 5(b)). Basically, as discussed above, there are two main ways of nitrile loss: scission of the grafted chain and concomitant loss of chain fragments due to the chemical attack, and conversion of the nitrile to amide and carboxyl groups as a result of hydrolysis. In the *post-mortem* analysis for the 130 h intermittent OCV test (Fig. 12), we can find that the calculated average degree of hydrolysis caused by testing in the styrene/AN co-grafted membrane is around 85%. It is found, however, that the hydrolysis is not homogeneous over the active area of the membrane. On the other hand, the hydrolysis of

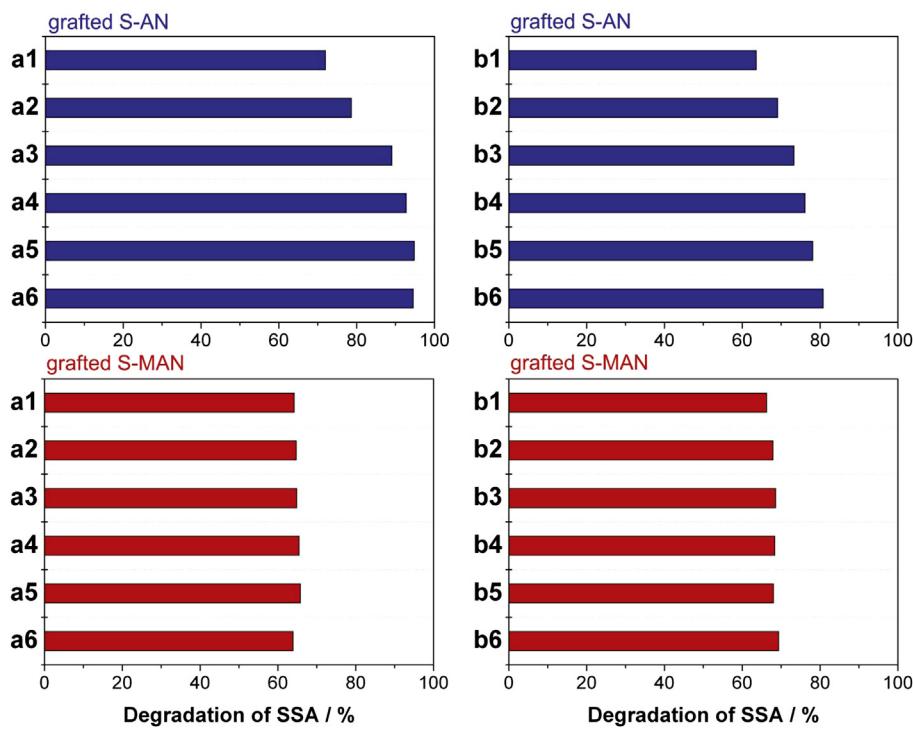


Fig. 13. Local degree of degradation of the grafted SSA units in the styrene/AN co-grafted membrane and the styrene/MAN co-grafted membrane, respectively, aged over 130 h in the intermittent OCV durability test.

the nitrile in the styrene/MAN co-grafted membrane is negligible, which can be confirmed by the fact that the degree of SSA degradation and the degree of nitrile loss are very consistent for the styrene/MAN co-grafted membrane. This suggests that the nitrile groups are detached from the backbone together with SSA groups without the impact of hydrolysis in the styrene/MAN co-grafted membrane. It also suggests that the presence of the α -methyl group in the MAN unit can protect the nitrile groups against hydrolysis in the fuel cell environment. The stabilizing effect of the α -methyl group is likely to be associated with both a steric hindrance effect and an electronic inductive effect of the methyl group, which is able to limit the attack of a nucleophile (here: H_2O) on the carbon of the $-\text{C}\equiv\text{N}$ unit and stabilize it due to its electron donating nature.

Interestingly, when comparing the data of the *post-mortem* analysis for the tested styrene/MAN co-grafted membranes, we can find a good agreement between the 130 h intermittent test (Fig. 12) and the 130 h continuous test (Fig. 6). The degrees of SSA degradation in both kinds of tests are the same, i.e., around 65%, regardless of the testing protocol. In addition, the degrees of nitrile loss in both kinds of tests also show a good agreement. In contrast, the tested styrene/AN co-grafted membranes do not exhibit an agreement of the *post-mortem* analysis for the 130 h intermittent test and the 130 h continuous test. In fact, during the 130 h intermittent OCV test, the intervals for cell performance and gas crossover measurements increase the time of hydrolysis of the membrane in the cell, which results in a more pronounced loss (95%) of nitrile groups, compared to the loss in the continuous test (83%). As discussed above, with the decreased fraction of nitrile units in the graft chains, the degradation of SSA units will be accelerated, leading to a higher extent of degradation of SSA units in the intermittent test (80%) than that in the continuous test (61%). Due to the improved resistance against hydrolysis, the tested styrene/MAN co-grafted membranes do not show different degradation behavior with the varied testing protocols.

The finding about the influence of the nitrile hydrolysis on membrane deterioration can provide us with a clue to explain the inhomogeneous in-plane degradation which occurred in the 130 h intermittent OCV test in case of the styrene/AN co-grafted membrane (Fig. 13). It is found that the areas close to the inlets of the reactant gases clearly show less degradation than the areas close to the outlets. This inhomogeneous in-plane degradation is responsible for a larger error bar shown for the degradation degree of SSA in the styrene/AN co-grafted membrane (Fig. 12). We speculate that the inhomogeneity is associated with an inhomogeneous in-plane distribution of hydrolysis, since the nitrile hydrolysis is a decisive factor in the context of membrane degradation. It is possible that, owing to effect of gravity, the areas close to the outlets, which are at the bottom of the cell, could accumulate more water than the areas close to the inlets of the reactant gases, which are at the top of the cell. The distribution of water thereby leads to different degrees of hydrolysis over the active area of the tested membrane, which in turn affects on the distribution of SSA decomposition. This hypothesis can be indirectly supported by a rather homogeneous degradation in the styrene/MAN co-grafted membrane (Fig. 13), which is not affected by hydrolysis.

4. Conclusions

The fuel cell performance of different types of styrene-based radiation grafted membranes on the basis of a fixed ion exchange capacity of around 1.5 mmol g^{-1} have been evaluated in a single H_2/O_2 fuel cell. The effect of nitrile-containing co-monomer on the chemical degradation of styrene-based radiation grafted membranes is investigated in a set of OCV tests. H_2 crossover rates are

measured *in situ* before and after testing. The deterioration of membranes is monitored online from the temporal evolution of high frequency resistance (HFR) and quantified in the *post-mortem* analysis based on transmission FTIR spectroscopy. Two types of nitrile-containing membranes are used to examine the role of each functional group on the co-monomer units and to gain an insight into the influence of nitrile hydrolysis.

Having a relatively lower membrane resistance and better interfacial properties, the styrene/MAN co-grafted membrane exhibits the closest performance to the Nafion[®] NR212 membrane among the tested radiation grafted membranes. The results demonstrate that both of styrene/MAN and styrene/AN co-grafted membranes have a significantly enhanced durability in comparison to the pure styrene grafted membrane under OCV conditions. The H_2 crossover measurements support the hypothesis of a stabilization mechanism where the enhanced chain stiffness and chain-to-chain binding introduced by the nature of the nitrile group can restrict the transport of reactant gases and membrane-degrading species through the membrane. It is observed that styrene/AN co-grafted membranes have a similar decomposition rate compared to the styrene/MAN co-grafted membranes, but are more prone to hydrolysis in the fuel cell test.

In the 130 h OCV intermittent tests, the styrene/MAN co-grafted membrane exhibits better durability than the styrene/AN co-grafted membrane. *Post-mortem* analysis for hydrolysis and degradation quantification and a further test with pre-hydrolysis confirm that the accelerated degradation of the styrene/AN co-grafted membrane is a direct result of significant hydrolysis of nitrile. The α -methyl group in the MAN unit improves the stability of the nitrile groups against hydrolysis in the fuel cell environment. Playing the role of a “stabilizer”, there appears to be a critical content of nitrile in the grafted chain below which the protective effect will wane and degradation of the membrane will be accelerated.

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Appendix A. Supplementary material

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2013.06.009>.

References

- [1] K.A. Friedrich, F.N. Büchi, Z.P. Li, G. Kiesgen, D.C. Leinhos, H.S. Rottengruber, R.C. Bowman, B.V. Ratnakumar, in: A. Züttel, A. Borgschulte, L. Schlapbach (Eds.), *Hydrogen as a Future Energy Carrier*, Wiley-VCH, Weinheim, 2008, pp. 335–414.
- [2] T. Yamaki, *J. Power Sources* 195 (2010) 5848–5855.
- [3] L. Bonorand, G.G. Scherer, L. Gubler, *PSI Electrochemistry Laboratory – Annual Report 2011, 2012*, pp. 5–6, <http://dx.doi.org/10.3929/ethz-a-007047464>.
- [4] A. Bhattacharya, B.N. Misra, *Prog. Polym. Sci.* 29 (2004) 767–814.
- [5] T.R. Dargaville, G.A. George, D.J.T. Hill, A.K. Whittaker, *Prog. Polym. Sci.* 28 (2003) 1355–1376.
- [6] L. Gubler, S. Alkan-Gürsel, G.G. Scherer, *Fuel Cells* 5 (2005) 317–335.
- [7] M.M. Nasef, E.-S.A. Hegazy, *Prog. Polym. Sci.* 29 (2004) 499–561.
- [8] G. Hübner, E. Roduner, *J. Mater. Chem.* 9 (1999).
- [9] S.M. Dockheer, L. Gubler, P.L. Bounds, A.S. Domazou, G.G. Scherer, A. Wokaun, W.H. Koppenol, *Phys. Chem. Chem. Phys.* 12 (2010) 11609.
- [10] L. Gubler, S.M. Dockheer, W.H. Koppenol, *J. Electrochem. Soc.* 158 (2011) B755–B769.
- [11] R.A. Assink, C. Arnold Jr., R.P. Hollandsworth, *J. Membr. Sci.* 56 (1991) 143–151.

- [12] J. Chen, U. Septiani, M. Asano, Y. Maekawa, H. Kubota, M. Yoshida, *J. Appl. Polym. Sci.* 103 (2007) 1966–1972.
- [13] S. Hasegawa, S. Takahashi, H. Iwase, S. Koizumi, N. Morishita, K. Sato, T. Narita, M. Ohnuma, Y. Maekawa, *Polymer* 52 (2011) 98–106.
- [14] J. Chen, M. Asano, T. Yamaki, M. Yoshida, *J. Power Sources* 158 (2006) 69–77.
- [15] L. Gubler, M. Slaski, F. Wallasch, A. Wokaun, G.G. Scherer, *J. Membr. Sci.* 339 (2009) 68–77.
- [16] H. Ben youcef, L. Gubler, A. Foelske-Schmitz, G.G. Scherer, *J. Membr. Sci.* 381 (2011) 102–109.
- [17] L. Gubler, M. Slaski, A. Wokaun, G.G. Scherer, *Electrochem. Commun.* 8 (2006) 1215–1219.
- [18] L. Bonorand, P. Reichel, J. Thut, L. Gubler, *PSI Electrochemistry Laboratory – Annual Report 2012, 2013*, pp. 9–10, <http://dx.doi.org/10.3929/ethz-a-007047464>.
- [19] H. Ben youcef, L. Gubler, S. Alkan-Gürsel, D. Henkensmeier, A. Wokaun, G.G. Scherer, *Electrochem. Commun.* 11 (2009) 941–944.
- [20] L. Gubler, L. Bonorand, J. Thut, G.G. Scherer, *PSI Electrochemistry Laboratory – Annual Report 2011, 2012*, pp. 17–18, <http://dx.doi.org/10.3929/ethz-a-007047464>.
- [21] H. Liu, F.D. Coms, J. Zhang, H.A. Gasteiger, A.B. LaConti, in: F.N. Büchi, M. Inaba, T.J. Schmidt (Eds.), *Polymer Electrolyte Fuel Cell Durability*, Springer Science + Business Media, New York, 2009, pp. 71–118.
- [22] R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.-i. Kimijima, N. Iwashita, *Chem. Rev.* 107 (2007) 3904–3951.
- [23] S. Kreitmeier, G.A. Schuler, A. Wokaun, F.N. Büchi, *J. Power Sources* 212 (2012) 139–147.
- [24] X.Z. Yuan, H. Li, S. Zhang, J. Martin, H. Wang, *J. Power Sources* 196 (2011) 9107–9116.
- [25] D.M. Bernardi, M.W. Verbrugge, *J. Electrochem. Soc.* 139 (1992) 2477–2491.
- [26] E. Endoh, S. Terazono, H. Widjaja, Y. Takimoto, *Electrochem. Solid State Lett.* 7 (2004) A209–A211.
- [27] H. Ben youcef, K. Jetsrisuparb, A. Waibel, L. Gubler, A. Wokaun, G.G. Scherer, *PSI Electrochemistry Laboratory – Annual Report 2010*, ISSN 1661-5379, 2011, pp. 7–8.*
- [28] D.E. Curtin, R.D. Lousenberg, T.J. Henry, P.C. Tangeman, M.E. Tisack, *J. Power Sources* 131 (2004) 41–48.
- [29] K. Jetsrisuparb, H. Ben youcef, A. Wokaun, L. Gubler, *J. Membr. Sci.* (2013), submitted for publication.
- [30] L. Gubler, N. Prost, S. Alkan-Gürsel, G.G. Scherer, *Solid State Ionics* 176 (2005) 2849–2860.
- [31] S.S. Kocha, J. Deliang Yang, J.S. Yi, *AIChE J.* 52 (2006) 1916–1925.
- [32] M. Inaba, T. Kinumoto, M. Kiriakie, R. Umebayashi, A. Tasaka, Z. Ogumi, *Electrochim. Acta* 51 (2006) 5746–5753.
- [33] H. Ben youcef, K. Jetsrisuparb, L. Gubler, A. Wokaun, G.G. Scherer, *PSI Electrochemistry Laboratory – Annual Report 2010*, ISSN 1661-5379, 2011, pp. 5–6.*
- [34] F.N. Büchi, B. Gupta, O. Haas, G.G. Scherer, *Electrochim. Acta* 40 (1995) 345–353.
- [35] Z. Zhang, Y. Buchmüller, A. Wokaun, L. Gubler, *ECS Electrochem. Lett.* (2013), submitted for publication.
- [36] C. Chen, T. Fuller, *ECS Trans.* 11 (2007) 1127–1137.
- [37] V.A. Sethuraman, J.W. Weidner, A.T. Haug, S. Motupally, L.V. Protsailo, *J. Electrochem. Soc.* 155 (2008) B50–B57.
- [38] K. Jetsrisuparb, PhD Thesis No. 21257, ETH Zurich, 2013.
- [39] M. Salame, *J. Polym. Sci. Polym. Symp.* 41 (1973) 1–15.
- [40] A.E. Barnabeo, W.S. Creasy, L.M. Robeson, *J. Polym. Sci. Polym. Chem. Ed.* 13 (1975) 1979–1986.
- [41] V.O. Mittal, H.R. Kunz, J.M. Fenton, *J. Electrochem. Soc.* 154 (2007) B652–B656.
- [42] Z. Zhang, K. Jetsrisuparb, B. Miserere-Janssen, A. Wokaun, L. Gubler, *PSI Electrochemistry Laboratory – Annual Report 2012, 2013*, pp. 16–17, <http://dx.doi.org/10.3929/ethz-a-007047464>.
- [43] F.N. Büchi, G.G. Scherer, *J. Electrochem. Soc.* 148 (2001) A183–A188.
- [44] M. Eikerling, Y.I. Kharkats, A.A. Kornyshev, Y.M. Volkovich, *J. Electrochem. Soc.* 145 (1998) 2684–2699.
- [45] F.D. Coms, H. Xu, T. McCallum, C. Mittelstaedt, *ECS Trans.* 50 (2012) 907–918.